Glass and Ceramics, Vol. 69, Nos. 3 – 4, July, 2012 (Russian Original, Nos. 3 – 4, March – April, 2012)

UDC 666.71.041.9:536.42

MECHANISM OF SOLID-PHASE TRANSFORMATIONS ACCOMPANYING FIRING OF LIGHT-TONE CERAMIC BRICK: THERMODYNAMIC SUBSTANTIATION

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Translated from *Steklo i Keramika*, No. 3, pp. 8 – 11, March, 2012.

The results of thermodynamic modeling of the solid-phase processes accompanying the firing of light-tone volume-colored ceramic brick based on refractory clay and an artificial fluxing agent are presented. X-ray diffraction studies of ceramic samples confirm the results of the thermodynamic calculations. Consistent patterns in phase formation occurring in ceramic brick prepared with an artificial fluxing agent are presented.

Key words: facing brick, artificial fluxing agent, refractory clay, thermodynamic analysis.

The theoretical aspects of volume-coloring technology for light-tone ceramic materials are examined in [1 – 4]. As a rule, a natural or technogenic carbonate-containing component is used as a lightening additive in ceramic mixes together with high-iron clays. The interaction of calcium oxide with clayey minerals and quartz, which are present in clays in the form of an impurity, results in the formation of phases with a high reflection coefficient [1 – 3]:

$$CaO + SiO_2 = CaO \cdot SiO_2;$$

$$CaO + Al_2O_3 \cdot 2SiO_2 = CaO \cdot Al_2O_3 \cdot 2SiO_2.$$

It has been proposed that clays with different chemical-mineralogical composition be used together with chalk and the mineralizer NaCl [3]. Articles were fired at 1000°C. It was noted that the mineralizer intensifies the lightening of a ceramic crock.

Calcium carbonate introduced as slag from the Novocherkassk State Regional Power Plant together with lithium-bearing wastes promotes the formation of light-tone phases and low-melting eutectic compounds that lower the firing temperature of articles. The following equations describe the phase-formation reactions [4]:

$$LiCl + CaCO_3 = CaCl_2 + LiCO_3;$$

$$2LiCl + Al_2O_3 \cdot 2SiO_2 + Fe_2O_3 + 2CaO = CaO \cdot Al_2O_3 \cdot 2SiO_2 + 2LiFeO_2 + CaCl_2.$$

Quartz, anortite and fassaite phases have been identified in lightened crock with the optimal composition, including 20% $CaCO_3$ and 0.2% LiCl. Hematite is absent in the phase composition of volume-colored crock; the authors attribute this to hematite inclusion in the glass phase. High water absorption (to 24.5%) is observed in fired samples of the ceramic.

Carbonates increase the water absorption of articles to more than 14.0%, which impedes their use for obtaining facing ceramic brick. A metallurgical by-product in which calcium oxide is present in the silicates can be considered as an alternative [5].

The objective of the present work is to perform a thermodynamic analysis of the solid-phase reactions that occur during firing of light-tone volume-colored ceramic brick fabricated using refractory clayey raw materials and an artificial fluxing agent, to determine the most likely mechanisms of crystallization of light-colored phases, and to confirm the results by means of x-ray diffraction.

The following reactions describe the mechanism of the formation of light-colored phases via the interaction of a clayey mineral with components of an artificial fluxing agent:

$$2CaO \cdot SiO_2 + Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O = CaO \cdot Al_2O_3 \cdot 2SiO_2 + CaO \cdot SiO_2 + 2H_2O\uparrow; \quad (1)$$

$$0.5(2CaO \cdot SiO_2) + 0.5(SiO_2) = CaO \cdot SiO_2; \quad (2)$$

$$0.273(3CaO \cdot 2SiO_2) + 0.091(2CaO \cdot SiO_2) + 0.363(SiO_2) = CaO \cdot SiO_2; \quad (3)$$

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$$3CaO\cdot 2SiO_2 + Al_2O_3\cdot 2SiO_2\cdot 2H_2O = CaO\cdot Al_2O_3\cdot 2SiO_2 + 2(CaO\cdot SiO_2) + 2H_2O\uparrow; \quad (4)$$

$$0.5(2CaO\cdot SiO_2) + Al_2O_3\cdot 2SiO_2\cdot 2H_2O = \frac{1}{9}(3Al_2O_3\cdot 2SiO_2) + \frac{1}{3}(CaO\cdot SiO_2) + \frac{2}{3}(CaO\cdot Al_2O_3\cdot 2SiO_2) + 2H_2O\uparrow + \frac{11}{18}SiO_2\ (\text{Amorph.}); \quad (5)$$

$$2CaO\cdot SiO_2 + \frac{1}{6}(3CaO\cdot 2SiO_2) + Al_2O_3\cdot 2SiO_2\cdot 2H_2O = \frac{1}{2}CaO\cdot Al_2O_3\cdot 2SiO_2 + 2(CaO\cdot SiO_2) + \frac{1}{6}(3Al_2O_3\cdot 2SiO_2) + 2H_2O\uparrow. \quad (6)$$

The ThermoGibbs program was used to perform the thermodynamic modeling of the reactions leading to the formation of light-colored phases. A particularity of this program is that all calculations are performed taking account of the polymorphic transformation of the initial substances and corrections are made in the equation $dG = f(T)$. This makes it possible to perform more accurate calculations. For the reactions (1) – (6) the equations for the change of the Gibbs energy were calculated taking account of the polymorphic transformations of the quartz and the phase transition $\gamma - 2CaO\cdot SiO_2 \rightarrow \alpha - 2CaO\cdot SiO_2$ at 810°C. As examples, the equations $dG = f(T)$ calculated for the reactions (1) and (2) are presented below:

$$dG_1 = 66{,}581.9200 - 43.0064T\ln T + 0.0397\times 10^{-3}T^2 + \frac{3{,}089{,}840}{T} + 1.2808\times 10^{-6}T^3 + 4.6608\times 10^{-6}T^4 - 107.7601T;$$

$$dG_2 = -35{,}200.9500 - 8.0890T\ln T + 5.9065\times 10^{-3}T^2 + \frac{1{,}412{,}175}{T} + 62.6371T.$$

The change of the Gibbs energy and the logarithm of the equilibrium constant in the temperature interval 100 – 1100°C are shown in Fig. 1.

As Fig. 1 evidences, heat is released in all reactions. The most likely reactions are reaction (1) (dG_{1000} = –429.2787 kJ/mole; $\ln(kp)_{1000} = 37.21$) and (4) (dG_{1000} = –473.0919 kJ/mole; $\ln(kp)_{1000} = 41.07$). Anortite and wollastonite phases should form as a result of solid-phase interactions occurring between the initial substances. Because of the high content of kaolinite primary mullite can form in the refractory clay component at temperatures above 1000°C via the reaction (6) ($dG_{1050} = -399.8728$ kJ/mole; $\ln(kp)_{1050} = 36.35$).

The VKS-2 refractory clay from the Vladimirovskoe deposit was used as the plastic component in the ceramic mixes.

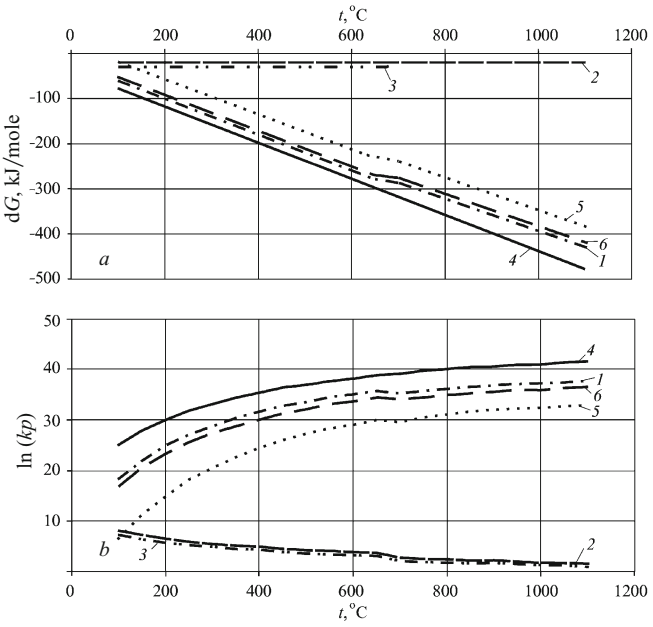

Fig. 1. Gibbs energy change dG (*a*) and the logarithm ln (kp) of the equilibrium constant (*b*) versus the temperature for the reactions (1) – (6). The curves are number according to the reaction.

Chemical Composition of VKS-2 Clay (wt.%)

SiO_2	59.63
Fe_2O_3	2.59
Al_2O_3	23.60
TiO_2	1.04
ΣRO	0.96
ΣR_2O	3.27
Other	8.08

An artificial fluxing agent developed for this purpose on the basis of ferrous and non-ferrous metallurgical slags was used as the fluxing component [6]. The chemical composition of the artificial flux is as follows (wt.%): 35.26 SiO_2; 3.66 Fe_2O_3; 7.08 Al_2O_3; 0.78 TiO_2; 30.50 CaO; 7.49 MgO; 7.90 (NaCl + KCl); 7.26 CaF_2. The artificial fluxing agent was prepared by combined comminution and mixing of steel-melting and aluminum slags.

The following mix composition was adopted to perform the experiments on determining the phase composition of the light-colored ceramic (wt.%): 85 — VKS-2; 15 — artificial fluxing agent. Ceramic samples were formed by the plastic method with moisture content 23%. The samples formed were first dried at room temperature and then in a desiccator at temperature 100 ± 5°C. The firing temperatures were 1000°C (composition 1B) and 1050°C (composition 2B); the isothermal soaking time was 1 h.

X-ray diffraction studies of sample 1B (Fig. 2*a*) showed the presence of p-quartz, anortite, wollastonite, and pyroxene phases. The following phases were identified in sample 2B (Fig. 2*b*): β-quartz, anortite, wollastonite and mullite. A he-

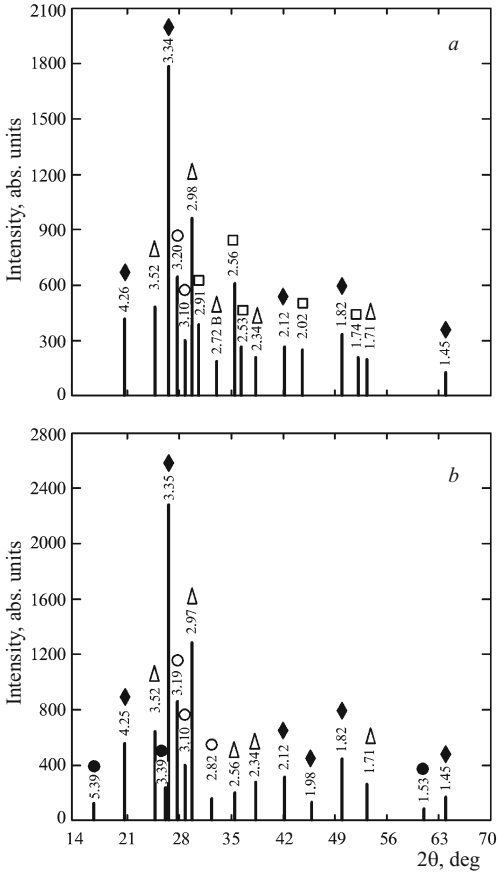

Fig. 2. Line diffraction pattern of ceramic 1B (*a*) and 2B (*b*) samples: ♦) quartz; △) wollastonite; ○) anortite; ●) mullite; □) pyroxene.

matite phase is absent in both compositions. This is because hematite enters into pyroxene and light-coloring crystalline phases — mullite and anortite — by means of the isomorphic substitution $Al^{3+} \rightarrow Fe^{3+}$ [7]. Most likely, fassaite Ca(Mg, Fe^{3+}, Fe^{2+}, Al)[(Si, $Al)_2O_6$] forms as pyroxene [8]. A feature of phase formation occurring when an artificial fluxing agent is used is that at temperatures to 1000°C pyroxene forms together with anortite and wollastonite. The diffraction peaks characteristic for pyroxene vanish at firing temperature 1050°C. Mullite peaks appear in the diffraction patterns, and the intensity of the diffraction peaks of anortite and wollastonite increases. Most likely, because a large amount of liquid phase forms at temperatures above 1000°C as a result of the presence of alkali-metal chlorides in the artificial fluxing agent the pyroxene dissolves in the melt.

In summary, the mechanism of phase formation during firing of light-tone ceramic brick obtained on the basis of refractory clay and an artificial fluxing agent was thermodynamically substantiated and experimentally confirmed. X-ray diffraction studies confirmed that the following light-colored phases are formed when a ceramic is fired — anortite and wollastonite, whose content at temperatures above 1000°C increases. Crystallization of pyroxene occurs at temperatures to 1000°C. Primary mullite forms when the firing temperature increases to 1050°C. The results of the thermodynamic modeling of the possible solid-phase reactions occurring during lightening of a ceramic crock showed that the most likely process leading to the formation of light-colored phases occurs via the equations (1), (4) and (6), characterized by large changes of the Gibbs energy: (dG^1_{1000} = –429.2787; dG^4_{1000} = –473.0919; dG^6_{1050} = –399.8729 kJ/mole).

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